spe

ANTEC® 2019
Detroit, MI • March 18-21, 2019
CO-HOSTED BY SPE DETROIT

ANTEC® 2019
PAPERS

HIGH DENSITY POLYETHYLENE BLENDS FOR ADDITIVE MANUFACTURING

Craig F. Gorin, Daniel L. Dermody, Scott T. Matteucci, Joseph Harris, Paul R. Vlasak, The Dow Chemical Company, Midland, MI
Jun Li, Sanjib Biswas, Nathan Wilmot, The Dow Chemical Company, Lake Jackson, TX

Abstract

High density polyethylene is challenging to use in standard additive manufacturing methods today, but would provide desirable properties such as chemical resistance, lightweighting, and durability to enable applications beyond prototyping. In this work, we describe high density polyethylene blends with highly branched polyethylene or polyethylene copolymers that improve adhesion and reduce warpage, significantly improving printability in standard filament extrusion 3D-printing methods.

Introduction

3D-printing, a sub-category of additive manufacturing (AM), is a rapidly growing field, enabling customizable parts with unique geometries and the potential for otherwise inaccessible properties. Today, 3D-printing is generally limited to "desktop" home and educational users or prototyping in industrial applications due to slow speed and poor material properties.[1] A variety of new printing technologies have been developed to increase printing speed such as Continuous Liquid Interface Production (CLIP) or Multi Jet Fusion (MJF) printing, however significant material property gaps remain when compared to traditional manufacturing methods.[2] Printable materials with a variety of physical properties are required to enable the conversion of computer files into physical objects that perform as designed. In this work, we demonstrate a material science approach towards improving the printability of high density polyethylene (HDPE), a material ubiquitous throughout the manufacturing world, but highly challenging to print today with common AM methods.

HDPE provides many material properties beneficial to moving AM beyond prototyping, including low density for lightweighting, excellent chemical resistance, durability, and low cost. However, standard grades of HDPE are not easily used in common AM methods. If utilized in filament extrusion printing methods, such as Fused Filament Fabrication (FFF), the resultant part will have poor adhesion and will severely warp. For powder sintering methods such as Selective Laser Sintering (SLS), polyolefins do not absorb energy in the relevant wavelengths and no sintering will occur. Finally, polyolefin polymerization is not amenable to vat photopolymerization methods such as Stereolithography (SLA) or CLIP.

In the AM literature, HDPE is mainly found in discussions for recycling. In several instances, small scale demonstrations of the conversion of waste HDPE, such as that found in milk jugs, to filament have been performed.[3] This filament is then extrudable in standard FFF printers, but generally produces parts with poor dimensional stability. HDPE filaments can also be found in the marketplace, however these are considered to be experimental with no reliable or reproducible conditions to enable high quality prints.[4] Finally, a small volume of work around the use of wood pulp or other fillers to enable printing of HDPE has been disclosed, but these fillers impact material properties.[5] In this work, we endeavored to produce printable HDPE by blending with polyethylene-based additives to reduce warpage and improve adhesion, without significantly impacting desired properties such as density and chemical resistance.

Materials and Experimental Methods

Several HDPE, linear low density polyethylene (LLDPE) and low density polyethylene (LDPE) resins manufactured by The Dow Chemical Company were utilized in this work. The melt indices (MI) for all resins were measured at 190 ºC (2.16 kg). Melting temperature (T_m) was measured by Differential Scanning Calorimetry by ramping from -80 to 200 °C at 10 °C/min. **HDPE-1** has an MI of 1.5 g/10min, a solid density of 0.955 g/cm^3, and a T_m of 130 °C. **HDPE-2** has an MI of 44 g/10min, a solid density of 0.951 g/cm^3, and a T_m of 128 °C. **LDPE-1** has an MI of 8.0 g/10min, a solid density of 0.918 g/cm^3, and a T_m of 105 °C. **LDPE-2** has an MI of 1.9 g/10min, a solid density of 0.919 g/cm^3, and a T_m of 108 °C. **LLDPE-1,** produced using metallocene catalyst, had an MI of 4.0 g/10min, a solid density of 0.919 g/cm^3, and a T_m of 122 °C. Finally, an ethylene acrylic acid (EAA) copolymer **EAA-1** produced by SK Global had 9.7% acrylic acid comonomer, an MI of 20 g/10min, a solid density of 0.938 g/cm^3, and a T_m of 95 °C.

Materials for chemical resistance testing including glacial acetic acid, nitric acid (70%), phosphoric acid (85%), ethanol, methanol, acetone, limonene, isopropanol, and propylene glycol were purchased from Fisher

Scientific. Petroleum was purchased from Millipore Sigma. Materials were diluted with deionized water as needed.

Polymers were melt blended using a Haake Polylab Micro 18 twin screw extruder at 150 °C and pelletized. The pellets were then formed into filaments by feeding the desired pellets into a single screw extruder heated to 190 °C with the screw turning at 10 rpms. The polymer melt was extruded through a 1.8 mm nozzle forming a filament having essentially the same diameter.

Initial parts were printed on a MakerBot Replicator 2X, which is commercially available from Stratasys Ltd, Minneapolis, Minn (USA). Small three dimensional boxes (with dimensions 2 cm x 2 cm x 1 mm) with layer height 0.2 mm with full infill were printed. Printer temperatures (unless otherwise described) were set to a bed temperature (coated with Aqua Net Hair Spray) of 110°C and a nozzle temperature of 210°C. Printing occurred at 10 mm/sec. Additional parts for chemical resistance testing were printed on a Hyrel 30M. Three dimensional sheets (with dimensions 100 mm x 100 mm x 0.8 mm) with layer height 0.2 mm, and 100% rectilinear infill were printed. Print bed is pretreated with polypropylene tape and set at 95°C, while the nozzle temperature is set at 210 °C.

Filament cross sections were analyzed by Scanning Electron Microscopy (SEM). A section of each filament was polished from core to skin at -90°C using a Diatome cryo 35 knife and a Leica UC7:FC7 ultramicrotome. After allowing the samples to come back to room temperature, they were vapor stained by suspension over a 0.5% ruthenium tetroxide solution for 1 hour. Samples were then carbon coated for conductivity and examined using a FEI Nova NanoSEM operating at 5 kv. Images were analyzed using ImageJ to obtain area percent, average length of major and minor axes and circularity (C) calculated as follows:

$$C = \frac{4\pi A}{P^2} \tag{1}$$

where A is the area (µm) and P is the perimeter (µm).

Dogbone tensile bars (3.8 cm x 1.5 cm, 0.5 cm test width) were punched according to ASTM D1708. Stress vs. Strain curves were obtained using a TA Instruments Texture Analyzer with a 50 kg load cell extended at 1.27 cm/min.

Results and Discussion

A review of the literature indicated HDPE filament was difficult to print. Initial exploration focused on validating and understanding the challenges for HDPE in FFF printing. Two HDPE resins, **HDPE-1** and **HDPE-2,**

with significantly different MI (1.9 and 44 respectively) were extruded into filaments. The filaments were loaded into the Makerbot printer, and printing of small 2 x 2 cm squares was attempted using various nozzle temperatures. It was found material would extrude from 160 to 250 °C, although brown scorch marks were observed on material printed above 230 °C. Material extruded most consistently with the nozzle set to 210 °C. Next, printer bed conditions including treatment with or without Aqua Net Hairspray, and temperature between 25 and 110 °C were explored. On bare glass, regardless of temperature, there was no adhesion of the extruded bead to the bed and no shape could be printed. With the hair spray treatment, adhesion of the first layer was significantly improved when the bed temp was > 70 °C. However, after the first layer was printed, the layer started to warp and curl. Attempts to continue printing were sometimes successful, although the final parts would end up significantly warped. At other times, the nozzle would hit the curled lower layers and pull material from its desired position. Examples of common print issues are shown in **Figure 1**. In general, the higher MI **HDPE-2** was more likely to complete a printed part, but warpage was consistently severe.
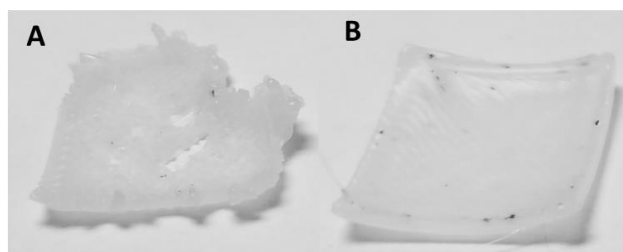

Figure 1. Example prints of **A**: **HDPE-1** and **B**: **HDPE-2** demonstrating printability issues of adhesion and warpage

Printing HDPE Blends

Initial experiments indicated poor adhesion and significant warpage were the major barriers to successful FFF printing of HDPE materials. Warpage was likely due to stresses imparted into the material during cooling and crystallization. In addition, poor adhesion was likely due to the low surface energy of HDPE. It was hypothesized polymer blends that modify the crystallinity of HDPE could reduce warpage while retaining desired properties of neat HDPE like chemical resistance, durability and density.

Polymers were blended using a twin screw extruder, extruded into filaments using a single screw extruder, and printed using the MakerBot using the optimal conditions of 210 °C nozzle temp, 110 °C bed temperature coated with hair spray identified in the previous section. Initial evaluation of printability of each blend is shown in **Table 1.** The calculated density (additive by weight) of the neat

resin or blend is shown for each material. In addition, it is noted whether the print was successfully completed or failed due to poor adhesion/warpage. Finally, warpage of parts that printed completely was quantified by placing the part flat on a table and measuring the height of the gap at each corner. Examples of printed parts with improved printability are shown in **Figure 2.**

Table 1. Densities and printability of HDPE blends

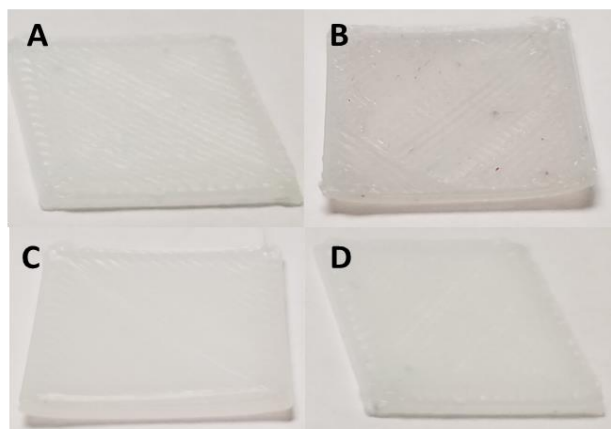| Material	Density (g/cm^3)	Completed Printing Full Part (Y/N)	Gap Height at Corner (mm)
HDPE-1	0.955	N	-
HDPE-2	0.951	Y	2.7 ± 0.3
99 : 1 HDPE-1 : LDPE-1	0..955	Y	2.6 ± 0.4
90 : 10 HDPE-1 : LDPE-1	0.951	Y	0.2 ± 0.2
95 : 5 HDPE-1 : LDPE-2	0.953	Y	0.6 ± 0.2
95 : 5 HDPE-1 : LLDPE-1	0.953	N	-
95 : 5 HDPE-2 : EAA-1	0.950	Y	0.7 ± 0.3
90 : 10 HDPE-2 : EAA-1	0.950	Y	0.1 ± 0.1
80 : 20 HDPE-2 : EAA-1	0.948	Y	0.0 ± 0.0

Figure 2. Example prints of **A**: **90:10 HDPE-1:LDPE-1**, **B**: **95:5 HDPE-1:LDPE-2**, **C: 95:5 HDPE-2: EAA-1**, and **D: 80:20 HDPE-2:EAA-1** demonstrating significantly improved printability as compared to HDPE.

First, blends of **HDPE-1** and **LDPE-1** at 1% and 10% by weight were printed and compared to HDPE alone at similar densities. As described previously, the lower density, and higher MI, HDPE had improved printability. The 1% blend with **LDPE-1**, while having limited impact on overall density, had a visible improvement on printability. 10% **LDPE-1** blends printed with minimal warpage, and showed significant improvement compared to the HDPE of similar density.

Additional blends of **HDPE-1** with 5% **LDPE-2** or 5% **LLDPE-2** were tested. While **LDPE-2,** with lower MI as compared to **LDPE-1**, still showed improvement in printability, addition of **LLDPE-1** had no visible improvement and was unable to complete a print of a simple square.

Finally, blends of **HDPE-2** with varying levels of an ethylene acrylic acid copolymer **EAA-1** were tested. It was hypothesized EAA would influence crystallinity in the same manner as LDPE, while the acrylic acid comonomer functionality would provide additional improvement in adhesion to the printing bed and between layers of printed polymer blend. Again, significant improvement of printability was observed. Increased levels of **EAA-1** correlated to improved printability.

These results validated the hypothesis that polymer blends could impact crystallization, and significantly improve printability by reducing warpage of HDPE. LDPE or EAA, both highly branched polymers with significant long chain branching formed through high pressure radical polymerization, provided improvement dependent on amount added. LLDPE blends, with significantly lower long chain branching, showed no improvement at 5% addition.

Characterization of HDPE Blend Filaments

The results in the previous section indicated polymer blends could enable improved printability. It was desired to further understand the mechanism. LLDPE is known in the literature to blend fully with the HDPE, with a single combined melting peak as measured by differential scanning calorimetry (DSC).[6] Therefore, the LLDPE blend is just slightly reducing the density and overall crystallinity of the blend, similar to changes between **HDPE-1** and **HDPE-2**, explaining why little impact was observed.

Alternatively, it is known in the literature that highly branched polyethylene like LDPE will not be fully miscible with HDPE, retaining separate melting peaks as measured by DSC.[7] EAA is expected to do the same. It is hypothesized the immiscible component was forming discrete domains within the HDPE phase, interfering with

the continuity and length scale of the crystalline domains, reducing the stress incurred during crystallization and therefore warpage. While imaging of LDPE within HDPE to confirm this hypothesis is difficult due to the similar chemical signature, EAA can easily be differentiated due to the polar functionality of the acrylic acid comonomer.

Cross sections of the **HDPE-2:EAA-1** blends were polished, stained to better differentiate the acrylic acid monomer, and imaged by SEM. **Figure 3** shows micrographs of the 5% EAA and 20 % EAA blends. At both concentrations, discrete near-spherical particles are observed within the continuous HDPE phase. Image analysis indicates particles were generally sub-micron, although smaller and more uniform at 20% **EAA-1** (**Table 2**.) Circularity is measured on a scale from 0 to 1, with 1 being a perfect circle.
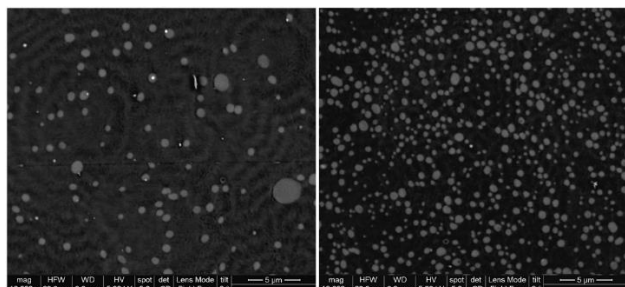

Figure 3. SEM images of **95:5 HDPE-2: EAA-1 (left)**, and **80:20 HDPE-2:EAA-1 (right)**. HDPE is dark gray while EAA is light gray due to staining**.**

Table 2. Analysis of EAA particles in HDPE blends

Material		Area (%)	Major Axis : Minor Axis (μm)	Circularity (0-1)
HDPE-2	**Mean (StDev)**	0	-	-
95 : 5 HDPE-2 : EAA-1	**Mean (StDev)**	4.4 (0.9)	0.7 : 0.6 (0.3 : 0.3)	0.90 (0.05)
80 : 20 HDPE-2 : EAA-1	**Mean (StDev)**	16.1 (1.5)	0.5 : 0.4 (0.2 : 0.2)	0.93 (0.19)

Characterization of 3D-Printed HDPE Blends

In the previous sections, we demonstrated blends of HDPE with significantly improved printability. However the overall goal of this work was to develop a 3D-printable version of HDPE to enable final parts with desirable properties including low density, excellent chemical resistance, and expected mechanical properties. LDPE or EAA blends retain the expected low density as compared to other high density fillers. However, it was not fully known whether chemical resistance would be maintained.

The 80:20 blend of **HDPE-2: EAA-1** contained the most secondary material by weight of the samples tested, as well as polar functionality from the acrylic acid conomoner, so had the highest potential for reduced chemical resistance. Therefore, chemical resistance testing was performed on 3D-printed parts of this blend, with the assumption that blends with reduced amount of EAA or LDPE would be less impacted.

To test mechanical and chemical resistance properties of a printed part, a large square 10 cm x 10 cm x 0.8 mm with 100% infill was printed on the Hyrel printer (cross-hatch pattern to provide layers with and against beads). These prints were then cut into 4 x 2.5 cm pieces to prevent edge effects. Three pieces were weighed, then immersed into one of several different acidic or organic solvent solutions. These solutions were chosen due to known gaps in chemical resistance for current materials used for FDM such as acrylonitrile-butadiene-styrene, polylactic acid or nylons.[8] After immersion for 24 hours at room temperature (except where noted), the samples were removed and washed with deionized water or isopropanol, allowed to dry for 10 minutes, then re-weighed.

While full mass data is not shown, only the samples immersed in limonene exhibited >1% change in weight, in this case increased weight due to absorption of the limonene, as expected for HDPE. This indicated there was minimal absorption or degradation of the HDPE blend in any of the other solvents.

The samples were then punched into dog bones for mechanical testing. Due to the rectilinear infill, the parts consisted of multiple layers with diagonal-aligned beads. Tensile strength measurements of samples after immersion are shown in **Figure 4** (end of paper), indicating retention of mechanical properties and excellent resistance to a variety of solvents and acids except limonene in agreement with the data above. The control sample, not immersed in any solvent, had an average tensile strength of 19.4 MPa. This indicated the HDPE blend printed part had a loss of tensile strength as compared to the expected 27 MPa of neat injection molded **HDPE-2**.[9] Generally, some loss of material properties is expected due to the layer-by-layer deposition process and incorporation of EAA, but significant strength remains.

Conclusions

To propel 3D-printing to applications beyond prototyping, printable materials with a variety of material properties are required. In this work, we demonstrated blends of HDPE with improved printability, enabling parts with excellent chemical resistance and low density for lightweighting. HDPE blends with highly branched LDPE or EAA polymers significantly improved printability by reducing warpage. EAA was found to form sub-micron, near-spherical particles within the continuous HDPE phase, hypothesized to be reducing the stresses incurred during crystallization. In the future, full characterization of impact of blending on strength, chemical resistance, and z-direction properties will be performed. Finally, we also envision expanding the use of polyolefins to powder printing methods.

Acknowledgements

References

1. T. Wohlers, I. Campbell. *Wohlers Report 2017*, Wohlers Associates, Inc. (2017)
2. S.C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mulhaupt, *Chem Rev*, **117,** 10212 (2017)
3. C. Baechler, M. DeVuono, J.M. Pearce. *Rapid Prototyp. J.*, **19**, 2 (2013)
4. "HDPE Filament – Natural", accessed 24 Sept. 2018, <https://filaments.ca/products/hdpe-filament-natural-1-75mm>
5. Y. Xiang et. al., C.N. 105295175A (2015)
6. C. Liu, J. Wang, J. He, *Polymer,* **43,** 3811, (2002)
7. Q. Fu, Y. Men, G. Strobl, *Polymer*, **44,** 1927 (2003)
8. "FDM Material Compatibility" Stratasys Inc., 2015.
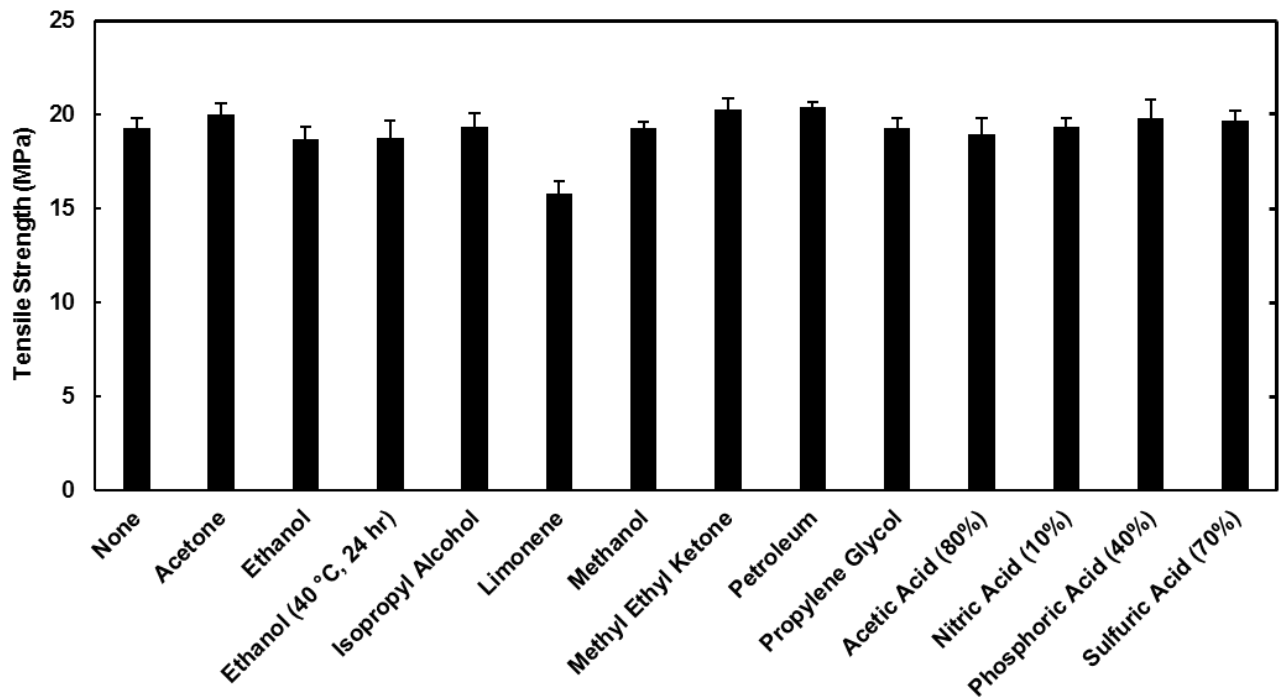9. "DMDA 8940-NT-7 Technical Information" The Dow Chemical Company, 2013.

Figure 4. Tensile strength of 3D-printed **80:20 HDPE-2:EAA-1** after immersion in solvent or acid solutions, demonstrating minimal loss of properties and excellent chemical resistance